Construction 0D/2D heterojunction by highly dispersed Ni$_2$P QDs loaded on the ultrathin g-C$_3$N$_4$ surface towards superhigh photocatalytic and photoelectric performance

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ABSTRACT

It is a hot topic to seek cheap and efficient cocatalyst to improve the activity of graphitic carbon nitride (g-C$_3$N$_4$) in photocatalytic water splitting to produce hydrogen and photoelectrochemical (PEC) performance. Herein, we prepared successfully the novel 0D/2D heterojunction by the modification of Ni$_2$P quantum dots (QDs) as co-catalyst on the surface of ultrathin g-C$_3$N$_4$ layer, which can greatly enhance the photocatalytic hydrogen production and PEC performance under visible light owing to the improvement of separation efficiency of photo-generated charge carriers and visible-light absorption capacity. Surprisingly, the optimum amount of Ni$_2$P loaded on the g-C$_3$N$_4$ is 3 wt%, whose hydrogen production rate is 1503 µmol h^{-1} g^{-1} being far superior to that of g-C$_3$N$_4$ decorated by 3 wt% Pt (560 µmol h^{-1} g^{-1}). Moreover, the photocurrent response value of Ni$_2$P/g-C$_3$N$_4$ photocatalyst is over 11 times and 3 times that of pure g-C$_3$N$_4$ and Pt/g-C$_3$N$_4$, respectively. What's better, the stable photocatalytic H$_2$ evolution and PEC performance of Ni$_2$P/g-C$_3$N$_4$ demonstrates its high stability and reusability resulting from Ni-N coordination on the surface of g-C$_3$N$_4$. This work provides valid evidence for the development of cheap, efficient and durable cocatalyst actting on the g-C$_3$N$_4$, opening up new opportunities and possibilities for dual function application.

1. Introduction

Under the present background of the increasing depletion of fossil fuels, the energy crisis seriously threatens the progress and development of human society. If renewable energy is not timely exploited as a substitute, social science and technology will be unavoidably restrained [1,2]. H$_2$ is admittedly recognized as renewable and clean energy, particularly significant for relieving global energy demand. Meanwhile, the photoelectrochemical (PEC) performance has also been widely researched in energy field [3]. For this situation, the photocatalytic technology is an effective means to actualize the preparation of hydrogen energy and improvement of photoelectric conversion efficiency, which has multiple advantages of low cost, non-pollution, mild reaction conditions as well as high stability [4]. At present, there have been a large number of literatures about the syntheses of various photocatalysts for enhanced photocatalytic and photoelectric performance [5]. But it is still a huge challenge and groping focus to find efficient, non-toxic, durable catalysts with dual functions such as photocatalysis water splitting for H$_2$ evolution and PEC performance.

In recent years, g-C$_3$N$_4$ has been widely reported as a commonly used non-metal organic photocatalyst under visible light owing to its suitable bandgap position, excellent stability, convenient preparation methods and so forth [6–10]. However, the photocatalytic and photoelectric activity of pure g-C$_3$N$_4$ is fairly low because of the rapid recombination of photogenerated electron-hole pairs, so it is necessary to construct the g-C$_3$N$_4$-based composite material. For example, pristine g-C$_3$N$_4$ can be combined with CdS [11], Bi$_3$TaO$_7$ [12] or Pt-Co alloy nanoparticle [13] into 2D/0D structure, with NiAl-LDH [14] or CPFA [15] into 2D/2D structure and with CdS/Rgo [16] into 2D/1D/2D structure. The construction of composite structure for g-C$_3$N$_4$ does enhance its photocatalytic hydrogen production performance and photoelectrochemical property, but there is still large space for improvement in terms of separating photon-generated carriers.

As we all know, the microscopic morphology and structure of materials are closely related with their properties, so it has become a common and effective modification method to construct unique compound structure for g-C$_3$N$_4$ [17–26]. Hence, quantum dots (QDs), as semiconductor nanocrystals, have been considered as one of the most

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potential structures to suppress recombination of photogenerated electron-hole pairs [27–31], settling for practical application in photocatalysis and photoelectricity [32,33]. Briefly speaking, the forceful quantum confinement derived from QDs is propitious to shorten the route length of photoexcited charge transmission [34–39]. On the one hand, faster charge transmission is able to increase hydrogen production rate. On the other hand, QDs may serve as source of photoelectric response to optical excitation. Nonetheless, there are few literatures about QDs modified g-C_3N_4 composites to improve photocatalytic and photoelectric performance. For instance, B. Babu etc. adopted solvothermal method to make SnO_2 QDs grow on the surface of g-C_3N_4 [40]; Junqi Li etc. employed oil-in-water self-assembly method to load Ag@AgCl QDs on g-C_3N_4 sheets [41]; Lihua Yao etc. utilized in-situ growth method to anchor $Cd_{0.5}Zn_{0.5}S$ QDs on g-C_3N_4 microribbons [42]. There is no doubt that the construction of 0D/2D heterostructure of QDs and g-C_3N_4 are beneficial to efficiently facilitate the activity of as-prepared photocatalyst. Most recently, a kind of transition metal phosphate, i.e. Ni_2P, has become an excellent cocatalyst for electrocatalysis and photocatalysis, inhibiting effectively the recombination of photogenerated charge carriers [43,44]. However, literatures about Ni_2P QDs as co-catalysts of ultrathin g-C_3N_4 layer have not been reported at present. Hence, it is reasonably conjectured that Ni_2P QDs decorated ultrathin g-C_3N_4 photocatalyst may tremendously enhance the photocatalytic hydrogen production activity and PEC performance.

In this work, the 0D/2D heterojunction photocatalyst has been successfully prepared by Ni_2P QDs embedded on the surface of ultrathin g-C_3N_4 layer. Under the same experimental conditions, the photocatalytic hydrogen production and PEC performance of Ni_2P/g-C_3N_4 will be superior to that of Pt/g-C_3N_4 with different content of cocatalyst, demonstrating noble-metal-free Ni_2P has the potential to replace the noble metal Pt. What's more, we gained an insight into this unique performance by light absorption, fluorescence and luminescent decay, etc. characterizations that significantly influenced factors on photocatalytic and PEC performance. Accompanied with detailed analyses of reaction mechanism, it is expected that our work will develop important insight on the highly active and low-cost catalyst for multiple applications.

2. Experimental section

2.1. Preparation and characterizations

Urea (AR, 99%), Nickel(II) acetate tetrahydrate ($Ni(OAc)_2\cdot4H_2O$, AR, 99%), NaOH (AR, 99%), NaH_2PO_2 (AR, 99%), $H_2PtCl_6\cdot H_2O$ (AR, 99%), Triethanolamine (AR, 98%) and N_2 (99.999%). All raw materials were purchased and used without further purification.

Graphitic carbon nitride (g-C_3N_4) nanosheets were prepared by the thermal polycondensation of urea with some modifications. Briefly, 20 g of urea was dried at 80 °C in the oven overnight. Then, dried urea was ground into powder in the agate mortar and put in a covered crucible. Next, the preprocessed urea was heated at 550 °C for 4 h with a heating rate of 2.5 °C/min. After cooling down, the light yellow product was washed in nitric acid solution (pH = 1) for 12 h, followed by washing with distilled water about 6 times. After being dried thoroughly, the resultant g-C_3N_4 product was further treated in a muffle furnace at 500 °C for 2 h with a heating rate of 2.5 °C/min.

Subsequently, 200 mg g-C_3N_4 was well-dispersed in 12 mL of deionized water. A varied amount of $Ni(OAc)_2\cdot4H_2O$ aqueous solution was added dropwise in the above miscible liquid with the mass fraction of Ni loading of 1, 3, 5 or 7%. After the mixed solution stirred for 3 h, a certain amount of NaOH (0.15 M) aqueous solution was added slowly on the basis of the Ni loading with a ratio of Ni: OH at 1:2, followed by magnetic stirring up to 1 h. The resultant mixture was heated at 80 °C with stirring by using an oil bath to evaporate the water. The obtained greenish yellow precursors were completely dried in a vacuum oven. Next, the solid precursor was ground with quantitative NaH_2PO_2 in the

agate mortar until uniformly mixed powder obtained. It was worth noting here that the mole ratio of Ni: NaH_2PO_2 was 1:10. Then, the mixture was placed in a covered crucible and heated in a tube furnace up to 300 °C and maintained for 4 h under N_2 atmosphere. After cooling down to the room temperature, the Ni_2P/g-C_3N_4 products were obtained and then kept in a dryer. Two contrast samples (i.e. Ni_2P and g-C_3N_4) were prepared through the same procedures. Ni_2P sample was synthesized without adding g-C_3N_4, while g-C_3N_4 was prepared without adding $Ni(OAc)_2\cdot4H_2O$ and NaH_2PO_2. For comparison, Pt/g-C_3N_4 was prepared through an in-situ photodeposition method according to previous literatures [45].

X-ray diffraction (XRD) scanned data were collected through a DX-2700 model X-ray diffractometer using Cu Ka radiation at a scan rate of 5°/min in the 2θ range of 10-80°, whose acceleration voltage and current were set at 40 kV and 30 mA, respectively. Fourier transform infrared spectroscopy (FTIR) was performed on a FT-IR Spectrometric Analyzer (Nicolet-560) using KBr powder. Morphology characterizations of the samples were surveyed by transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2100 F). The X-ray photoelectron spectroscopy (XPS) was performed by using a Thermo ESCALAB 250X (America) electron spectrometer using 150 W Al Kα X-ray sources and the peak positions were corrected against C 1 s peak (284.6 eV) from the adventitious carbon. UV–vis diffuse reflectance spectra (DRS) were measured on a HITACHIU-3900 UV–vis spectrophotometer. The Brunauer-Emmett-Teller (BET) specific surface area was calculated using the adsorption data and the average pore size was determined by the Barret–Joyner–Halenda method. The photoluminescence (PL) spectra and fluorescence decay spectra were recorded on a FLUOROMAX-4C-TCSPC at room temperature.

2.2. Photocatalytic activity experiments

The photocatalytic reaction was measured in a closed system (total volume about 100 mL). The Ni_2P/g-C_3N_4 catalyst (20 mg) was dispersed in aqueous solution of TEOA (20 vol%, pH = 11.4, 20 mL). Then, the reactor had to be bubbled with Ar gas for 15 min to remove air. A 300 W xenon lamp with a 420 nm cutoff filter was used as the visible light source. The photocatalytic reaction of Pt/g-C_3N_4 was conducted under the same condition except beginning with 20 mg g-C_3N_4 and a unique amount of $H_2PtCl_6\cdot H_2O$ aqueous solution followed by photodeposition of Pt cocatalyst. The amount of H_2 generated was determined using an online gas chromatography system. The AQE was measured under the same conditions except replacing the 420 nm cutoff filter with a band pass interference filter centered at 400, 420, 450, 500, 550, and 600 nm, respectively, during the 2nd hour of the reaction.

2.3. Photoelectrochemical measurements

The photoelectrochemical properties were measured in the VersaSTAT3 electrochemical working station employing a standard three-compartment cell under visible light assembled by a 300 W Xe lamp with a filter (λ > 420 nm). The as-prepared photocatalysts on the ITO glass (2 × 2 cm), the Pt plate and Ag/AgCl electrode were employed as the working electrode, counter electrode and the reference electrode, respectively. The above standard three-electrode cell was constituted to study the PEC property.

3. Results and discussion

3.1. Structure and morphology representation of the as-prepared photocatalysts

The structure and composition of the as-prepared photocatalyst are first investigated by XRD characterization. As can be seen in Fig. 1, the pure g-C_3N_4 has two diffraction peaks at 27.4° and 13.0° corresponding
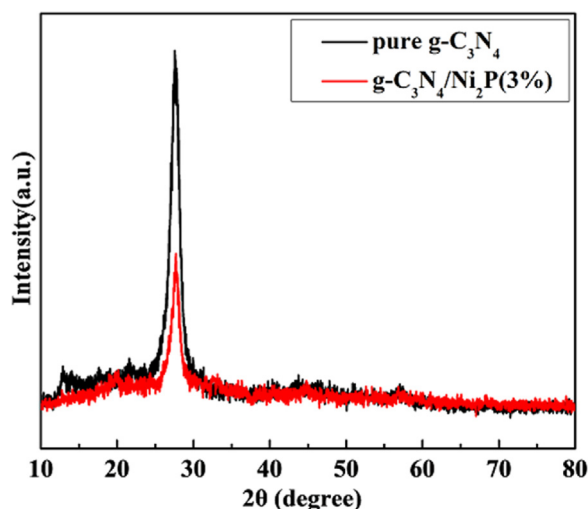
Fig. 1. XRD patterns of pure g-C$_3$N$_4$ and g-C$_3$N$_4$/Ni$_2$P-3% samples.

to the (002) and (100) planes of g-C$_3$N$_4$ with graphitic structure (JCPDS#87-1526), respectively [46]. Then, the diffraction peak position from g-C$_3$N$_4$ is not obviously changed before and after Ni$_2$P loading. However, the main diffraction peak of Ni$_2$P/g-C$_3$N$_4$ at 27.4°is pronouncedly weakened, which is potentially due to the structural decoration of Ni$_2$P QDs on g-C$_3$N$_4$ nanosheets through chemical binding. Noticeably, XRD result reveals that the doped Ni$_2$P cocatalyst does not incur any impure peaks on the structure of g-C$_3$N$_4$ catalyst, which implies that the Ni element maybe chemically bond with the g-C$_3$N$_4$ catalys [47]. Moreover, the same XRD characterization method is carried out for g-C$_3$N$_4$/Ni$_2$P composites with different loading amounts of Ni$_2$P cocatalyst and similar results are observed (Fig. S1). Nonetheless, with the increasing loading content of Ni$_2$P, the diffraction peak at 27.4°of g-C$_3$N$_4$ photocatalyst is markedly found to be weaker, which may origin from the Ni-N coordination on the surface of g-C$_3$N$_4$ in agreement with the above analysis.

Fig. S2 reveals fourier transform infrared (FT-IR) sepctra of Ni$_2$P/g-C$_3$N$_4$ composites as well as pure g-C$_3$N$_4$. As respect to pure g-C$_3$N$_4$ and g-C$_3$N$_4$/Ni$_2$P, the presence of a wide adsorption band between 800 and 1800 cm^{-1} is related to the polymerization structure of g-C$_3$N$_4$ due to the vibration characteristic of triazine ring and heptazine heterocyclic ring. The wide band ranging from 3000-3400 cm^{-1} involve uncondensed amino groups (−NH) and hydroxyl group (−OH) of the surface-adsorbed H$_2$O. In addition, no obvious signal about the formation of P−N or P−C bond is observed, suggesting that P element is not doped into the structure of g-C$_3$N$_4$. Particularly, similar FT-IR information is also characterized in g-C$_3$N$_4$/Ni$_2$P photocatalyst with Ni$_2$P loading, illustrating those g-C$_3$N$_4$/Ni$_2$P composites maintain the same structure as pure g-C$_3$N$_4$ and no produced other impurity peaks. This result is in great accordance with XRD analysis.

In order to have a thorough insight into the microscopic morphology of Ni$_2$P/g-C$_3$N$_4$ photocatalyst, the microstructural analyses were necessarily performed and the results are shown in Fig. 2. The transmission electron microscopy (TEM) images present the typical 2D nanosheet structure of g-C$_3$N$_4$ (Fig. 2a). It also displays ultrathin structural features observed from the edge of g-C$_3$N$_4$ nanosheet. By contrast, as is shown in the bright and dark field TEM images (Fig. 2b–c), Ni$_2$P QDs are distinctly observed on the surface of g-C$_3$N$_4$ nanosheets, validating the existence of Ni$_2$P cocatalyst as sufficient surface active sites. Especially, the sizes of all Ni$_2$P nanoparticles are smaller than 10 nm. Therein nanoparticles ranging from 4 to 5 nm account for the highest proportion of 30.3%. Additionally, the high resolution TEM (HRTEM) image (Fig. 2d) clearly indicates the close connection between Ni$_2$P QDs and g-C$_3$N$_4$ nanosheets. The more detailed HRTEM image (Fig. 2e) shows the distinct lattice fringes with an

interplanar spacing of 0.273 nm, which agrees well with the (200) plane of Ni$_2$P. Lastly, the corresponding elemental mapping images of Ni$_2$P/g-C$_3$N$_4$ photocatalyst (Fig. 2f–i) further confirm the homogeneous distribution of the elements Ni and P on the surface of g-C$_3$N$_4$ catalyst. There is no other obvious compositional distribution among the whole architecture. These results further prove that the Ni$_2$P QDs has been anchored on the g-C$_3$N$_4$ surface uniformly without generating any impurities, which are in line with the analyses of XRD and FT-IR.

Furthermore, the elements and surface chemical states of photocatalysts were researched by X-ray photoelectron spectroscopy (XPS). The XPS spectra of g-C$_3$N$_4$ and Ni$_2$P/g-C$_3$N$_4$ (Fig. 3a) verified that C, N were the co-owned and predominant elements, while Ni and P were the unique elements of the as-prepared Ni$_2$P/g-C$_3$N$_4$ catalyst, which indicates Ni$_2$P/g-C$_3$N$_4$ photocatalyst has been successfully synthesized. The high-resolution N 1 s spectrum of g-C$_3$N$_4$ (Fig. 3b) was decomposed into three peaks at 397.1 eV, 399.0 eV and 403.0 eV, which can be assigned to sp^2-hybridized nitrogen in triazine rings (C−N=C), tertiary nitrogen (N-(C)$_3$) groups, and positive charge localization in heterocycles (C−NH), respectively [48]. It is worth noting that the N 1s peak of tertiary nitrogen groups in Ni$_2$P/g-C$_3$N$_4$ located at 398.8 eV decreases by 0.2 eV compared to that in g-C$_3$N$_4$, which implies the combination of chemical bonds between Ni$_2$P QDs and g-C$_3$N$_4$ layer to form N−Ni bond. In contrast, there is no change at the N 1s peak of triazine rings located at 397.1 eV. Therefore, it is believed that Ni element can just interact with N element in tertiary nitrogen groups. More precisely, the electrons in triazine rings from N and C atoms have formed π bonds, not further forming bonds with Ni atoms. In term of Ni 2p spectrum (Fig. 3c), there are two predominant peaks at 855.3 and 874.0 eV corresponding to Ni 2p$_{3/2}$ and Ni 2p$_{1/2}$ in Ni$_2$P [49], while the peak at 860.1 eV is just the accompanied peak of Ni 2p$_{3/2}$ [50]. Fig. 3d gives the high resolution XPS spectrum of P 2p and the peak at 129.7 eV is a sign of Ni-P bonds [51]. In short, g-C$_3$N$_4$ catalyst has formed chemical bonds with Ni$_2$P cocatalyst in Ni$_2$P/g-C$_3$N$_4$ composite.

3.2. Photocatalytic and photoelectric performance over the as-prepared photocatalysts

We apply the as-prepared photocatalysts to water splitting for H$_2$ evolution under visible light. As is vividly illustrated in Fig. 4a, with the loading of Ni$_2$P on g-C$_3$N$_4$, the H$_2$ evolution activity of hybrids Ni$_2$P/g-C$_3$N$_4$ have drastically been enhanced (λ > 420 nm), while pure g-C$_3$N$_4$ can just produce 12.5 μmol h^{-1} g^{-1} of H$_2$. Fortunately, with 1% (1 wt% of Ni) of Ni$_2$P loading, the H$_2$ evolution rate can be remarkably increased to 1069.5 μmol h^{-1} g^{-1}. What's better, the H$_2$ evolution rate of 1503 μmol h^{-1} g^{-1} is reached at 3% of Ni loading, which has been the drastically high value reported so far. Nevertheless, the H$_2$ evolution rate is evidently decreased with higher loadings of Ni$_2$P, because of the shielding of the light absorption by excess Ni$_2$P in the reaction system [52]. Noticeably, the highest H$_2$ evolution rate of Ni$_2$P/g-C$_3$N$_4$ is closely three times that of the optimized Pt/g-C$_3$N$_4$ (560 μmol h^{-1} g^{-1}). To conclude, the photocatalytic hydrogen production performance of the prepared photocatalyst is improved remarkably superior to Pt/g-C$_3$N$_4$ catalyst, claiming that Ni$_2$P QDs is promising to replace noble metal Pt as cocatalyst of g-C$_3$N$_4$. Additionally, the apparent quantum efficiency (AQE) was measured under the same conditions of the reaction by merely changing band pass filters with different wavelengths. In the Fig. 4b, we can find that both quantum efficiency and optical absorption curve decrease with the increase of light wavelength. A relatively high AQE of 4.8% at 400 nm is achieved by g-C$_3$N$_4$/Ni$_2$P-3% photocatalyst.

Considering the practical application of Ni$_2$P/g-C$_3$N$_4$ photocatalyst, its stability is also a very crucial factor. As is clearly demonstrated in Fig. 5a, the H$_2$ generation rate of Ni$_2$P/g-C$_3$N$_4$ displays negligible reduction after five runs, illustrating that Ni$_2$P/g-C$_3$N$_4$ has eminent stability. In order to further confirm the stability and reusability of photocatalyst, the g-C$_3$N$_4$/Ni$_2$P(3%) sample after cyclic reaction was
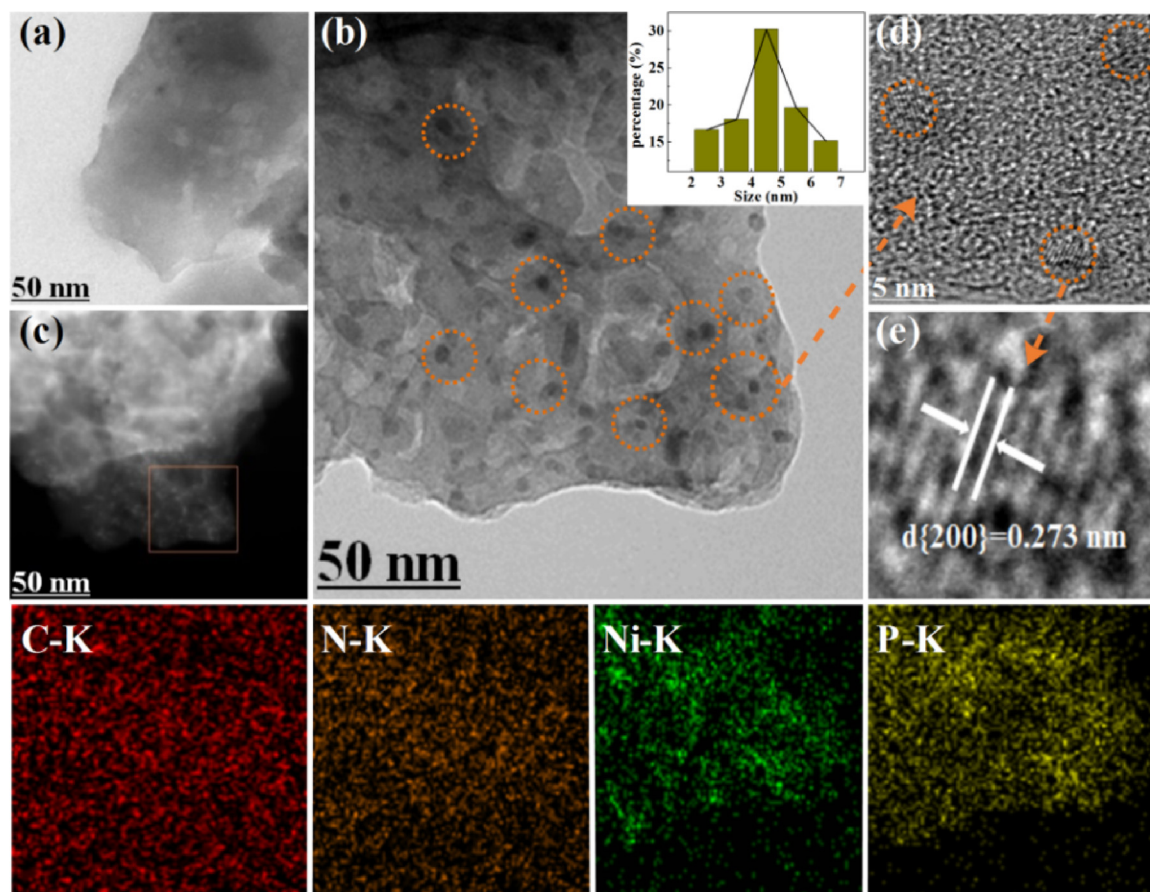
Fig. 2. TEM image of pure g-C$_3$N$_4$ (a), Bright field (b) and dark field (c) TEM images of g-C$_3$N4/Ni$_2$P and size distribution (inset of b), HRTEM images (d and e) and STEM-EDX elemental mapping (f–i) of g-C$_3$N$_4$/Ni$_2$P.

characterized again through the transmission electron microscopy (TEM). Obviously, the microstructure of g-C$_3$N$_4$/Ni$_2$P photocatalyst has not been changed at all in Fig. 5b because plenty of Ni$_2$P QDs are still attached to the surface of the ultrathin g-C$_3$N$_4$ nanosheet. All the above results prove the as-prepared 0D/2D photocatalyst can satisfy the condition of practical application because of high stability and reusability.

Besides superhigh hydrogen production performance, PEC properties of as-synthesized Ni$_2$P/g-C$_3$N$_4$ photocatalyst can also be evaluated for practical application. As a main indicator for photoresponse, photocurrent(I) reflects the generation of electron-hole pairs under the irradiation of visible light. Hence, PEC I-t curves are employed to study the interfacial charge separation efficiency and mobility for the photocatalysts under the periodic illumination of 30 s. Seen from Fig. 6a, the measured current value of pristine g-C$_3$N$_4$ is 7.48 μA while that of Ni$_2$P/g-C$_3$N$_4$ composite is 82.58 μA under the potential of 0.7 V vs. Ag/AgCl. The photocurrent value of Ni$_2$P/g-C$_3$N$_4$ photocatalyst is over 11 times that of bare g-C$_3$N$_4$, which unveils that the photo-reduction and photo-oxidation activity of g-C$_3$N$_4$ is drastically boosted for the construction of Ni$_2$P/g-C$_3$N$_4$heterojunction, benefiting the enhancement of PEC performance. Surprisingly, the current value of Ni$_2$P/g-C$_3$N$_4$ is 3.3 times that of Pt/g-C$_3$N$_4$ (25.02 μA), showing the probability of low-cost metals as cocatalysts of g-C$_3$N$_4$ in replacement of noble metals in PEC property. Furthermore, the photocurrent formed by the Ni$_2$P/g-C$_3$N$_4$ catalyst is much very stable and durable, beneficial for the practical application. Moreover, EIS measurement can provide the valid evidence for the mobility of electrons at the interfacial of solid electrode, and the results are displayed in Fig. 6b. The diameter of EIS Nyquist plots for g-C$_3$N$_4$/Ni$_2$P is far smaller than pure g-C$_3$N$_4$ and Pt/g-C$_3$N$_4$, which demonstrates that Ni$_2$P/g-C$_3$N$_4$ photocatalyst possesses less charge

migrate resistance at the interfacial electrolyte solution [53,54], thus displaying the excellent photocatalytic and photoelectric activity.

Fig. 7 shows I−t curves of Ni$_2$P/g-C$_3$N$_4$ composite under various monochromatic light irradiation including 400 nm, 420 nm, 450 nm, 500 nm, 550 nm and 600 nm. In particular, photocurrent response of Ni$_2$P/g-C$_3$N$_4$ is clearly observed at different wavelengths and the obtained results correspond to the information of AQE in Fig. 4b, which reveals the consistency of photocatalytic and photoelectric properties of Ni$_2$P/g-C$_3$N$_4$ photocatalyst. Therefore, 0D/2D heterojunction structure of Ni$_2$P/g-C$_3$N$_4$ composite greatly enhances photoelectric activity and stability of g-C$_3$N$_4$ photocatalyst, which is very benefit for practical applications.

3.3. The influence factors of enhanced photocatalytic and photoelectric activity

For investigating the effect of Ni$_2$P loading on g-C$_3$N$_4$ layers, the optical absorption property of Ni$_2$P/g-C$_3$N$_4$ photocatalyst is analyzed by UV–vis DRS. In Fig. 8a, both pure g-C$_3$N$_4$ and Ni$_2$P/g-C$_3$N$_4$ photocatalysts have the same absorption edge (426 nm), determining that the bandgap of g-C$_3$N$_4$ is not changed at all after modification of Ni$_2$P and ruling out the doping of Ni and P atoms into g-C$_3$N$_4$. To be precise, according to the intercept of the tangents to the plots of $(\alpha h\nu)^{1/2}$ vs photon energy, g-C$_3$N$_4$ and Ni$_2$P/g-C$_3$N$_4$ have the same energy gap (Eg) value (2.68 eV). As depicted in the Fig. S3, the band gaps measured herein are consistent with the reported literature values ($\approx$2.7). Furthermore, the absorption curve of Ni$_2$P/g-C$_3$N$_4$ photocatalyst extends to the visible light range up to about 700 nm, which is helpful to improve photocatalytic activity. This result is also corresponding to the results of AQE and photocurrent under different monochromatic light. In
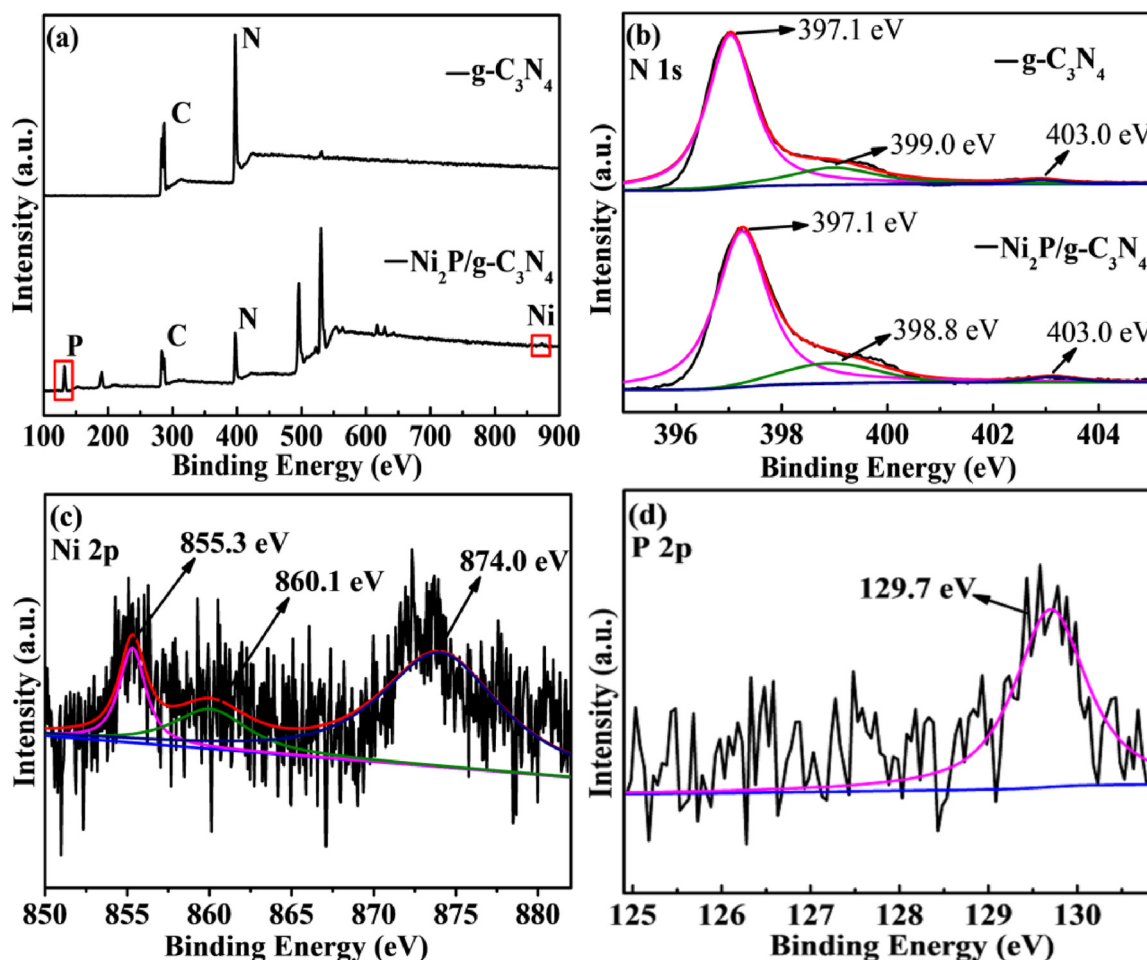
Fig. 3. XPS spectra of g-C_3N_4 and g-C_3N_4/Ni_2P: survey spectrum (a), N 1 s (b), Ni 2p (c) and P 2p (d).

addition, we can find the valence band value of pure g-C_3N_4 is 1.48 eV in Fig. 8b. Amazingly, the VB value (1.10 eV) of g-C_3N_4 in Ni_2P/g-C_3N_4 shifts up 0.38 eV, which implies that the conduction band (CB) value of g-C_3N_4 also has the up-shift owing to the unchanged bandgap value. As a consequence, photocatalytic H_2 production performance and photocurrent response of g-C_3N_4 are obviously enhanced.

In addition, the Brunauer-Emmett-Teller (BET) specific surface area and pore diameter distribution are also the important parameters for photocatalyst. As can be seen in Fig.9, the hysteresis loops of measured

isotherms appear between 0.4 and 1.0 (P/P_0), which corroborates the presence of mesopores (2–50 nm) in the g-C_3N_4 and Ni_2P/g-C_3N_4 samples. Also, the above consequence is confirmed by pore diameter distributions (inset in Fig. 9) with two peaks of mesoporous. In addition, the specific surface area of Ni_2P/g-C_3N_4 (18.37 $m^2\,g^{-1}$) is distinctly lower than that of pure g-C_3N_4 (41.1 $m^2\,g^{-1}$). Therefore, the effects of those factors on improved photocatalytic H_2 generation ability of g-C_3N_4 and Ni_2P/g-C_3N_4 samples are insignificant and neglectful. As a consequence, it further indirectly attests the enhanced
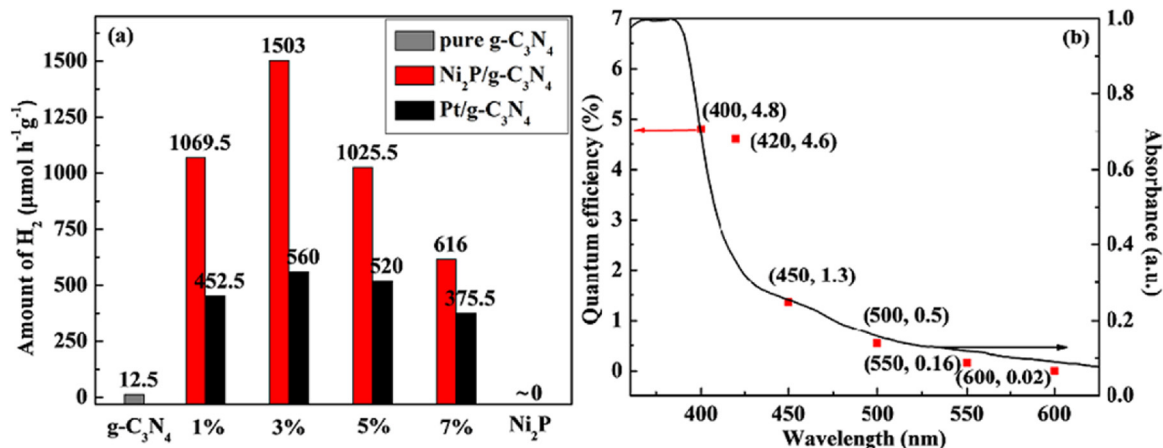

Fig. 4. Photocatalytic H_2 evolution rates over various samples under visible light (λ > 420 nm) (a); Apparent quantum efficiency and optical absorption curve of Ni_2P/g-C_3N_4 (b).
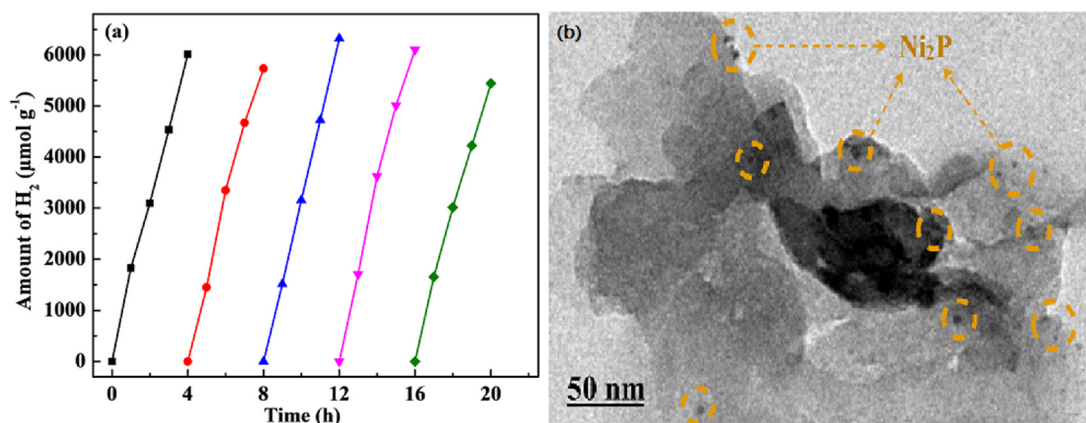
Fig. 5. Time-circle experiment of photocatalytic H$_2$ evolution over the Ni$_2$P/g-C$_3$N$_4$ sample (a), TEM image of Ni$_2$P/g-C$_3$N$_4$ sample after recycling experiment (b).

photocatalytic activity is ascribed to the effectively transferred and separated efficiency of charge carriers.

Generally speaking, photoluminescence spectra (PL) can reflect the charge separation behavior because higher PL intensity corresponds to lower photocatalytic activity. From Fig. 10a, the PL intensity is descended remarkably at approximately 450 nm after decorating Ni$_2$P QDs on the g-C$_3$N$_4$ surface, resulting in the fast transfer of electrons between g-C$_3$N$_4$ and Ni$_2$P in virtue of Ni-N bonds, which leads to the PL quenching as well as decrease of electron-hole recombination rate. As a result, the improvement of the photon-generated carrier separation efficiency promotes the enhancement of photocatalytic and photo-electric properties. In Fig. 10b, the fluorescent lifetime (1.33 ns) of Ni$_2$P/ g-C$_3$N$_4$ is shorter than that (2.58 ns) of pure g-C$_3$N$_4$, implying that an additional non-radiative decay channel may be created through the charge separation [55], which is in accordance with our steady-state PL quenching measurements.

3.4. Possible photocatalytic and photoelectric reaction mechanism

Based on the above investigation, the possible mechanism of pho-tocatalysis and photoelectricity of g-C$_3$N$_4$/Ni$_2$P will be analyzed in Fig. 11. Under the visible light irradiation, photo-generated carriers can separate and form electrons and holes in the conduction band (CB) and valence band (VB), respectively. Electrons in the CB are transferred to Ni$_2$P and react with water to produce hydrogen (H$_2$). Meanwhile, holes in the VB are neutralized by 20 vol% triethanolamine. With the assist of the Ni$_2$P cocatalyst, hydrogen production rate of g-C$_3$N$_4$ catalyst has been greatly increased. In addition, the photoinduced electrons are
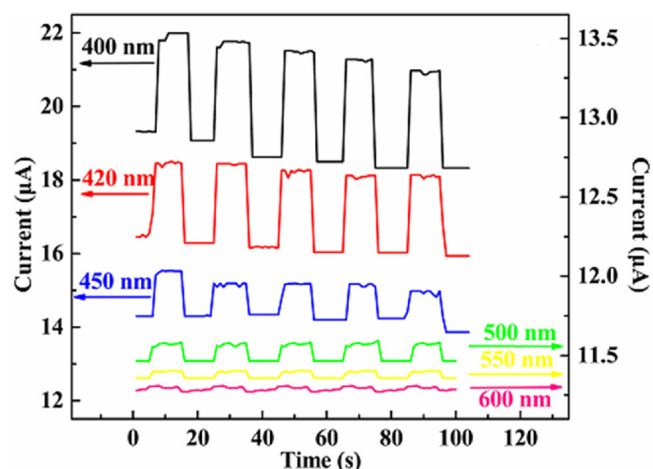

Fig. 7. The periodically illuminated photocurrent − time curves of 3% Ni$_2$P/g-C$_3$N$_4$ at different wavelengths.

transferred efficiently from the g-C$_3$N$_4$ to the ITO glass substrate via Ni$_2$P cocatalyst, and then transferred to the counter electrode (Pt sheet) through the external circuit, triggering the formation of photocurrent (I μA) in PEC tests. The photocurrent enhancement of g-C$_3$N$_4$/Ni$_2$P is ascribed to the high separation efficiency of the photoexcited electron-hole pairs after Ni$_2$P QDs loading. The formation of nickel-nitrogen bond (Ni-N) firmly fix Ni$_2$P QDs on the surface of g-C$_3$N$_4$ layers, en-ormously improving light absorption and efficiently boosting the
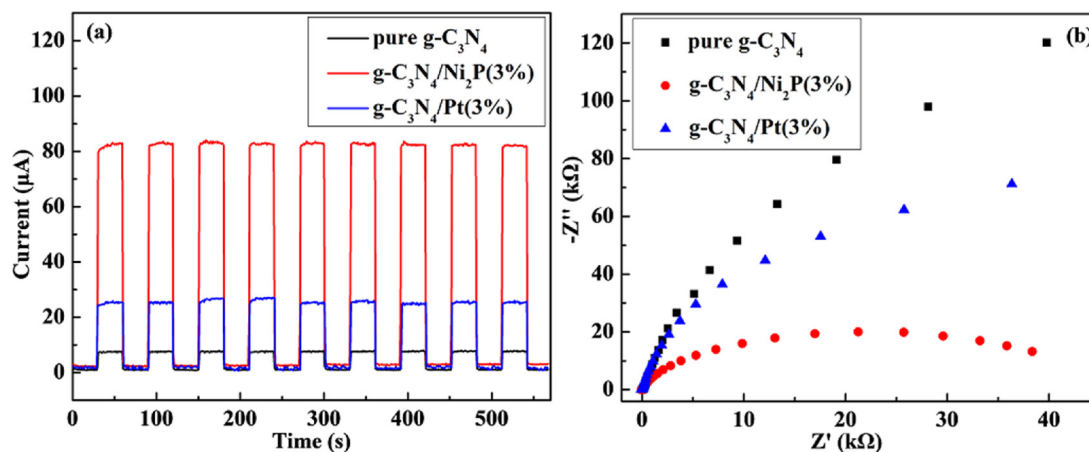

Fig. 6. The transient photocurrent − time (I − t) responses (a) and EIS Nyquist plots (b) of pure g-C$_3$N$_4$, g-C$_3$N$_4$/Ni$_2$P-3% and g-C$_3$N$_4$/Pt-3% in 0.5 M Na$_2$SO$_4$ solution.
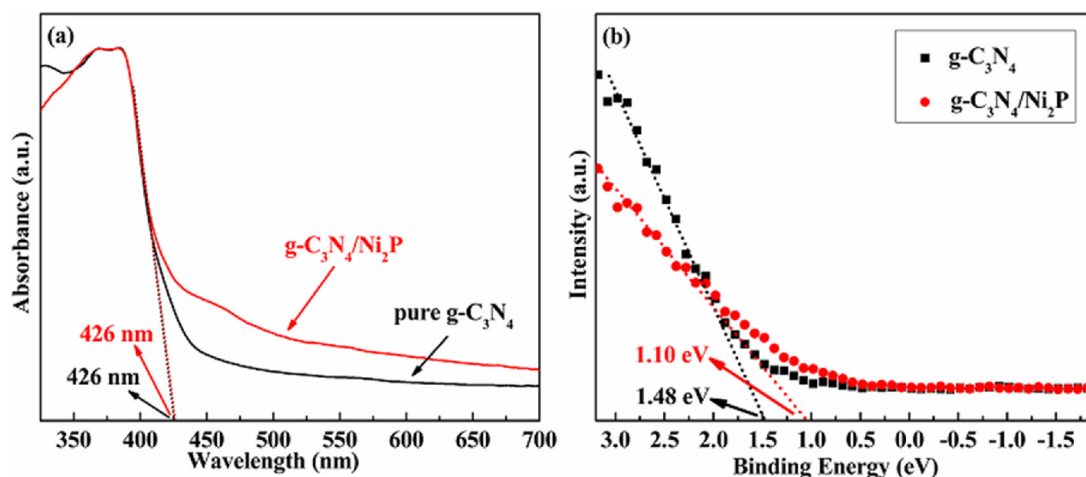
Fig. 8. UV–vis DRS spectra (a) and XPS valence band spectra (b) of g-C$_3$N$_4$ and g-C$_3$N$_4$/Ni$_2$P-3% samples.
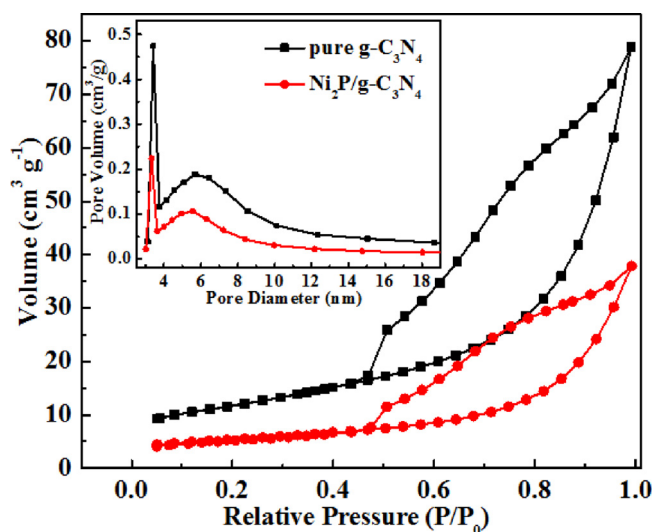

Fig. 9. N$_2$ adsorption–desorption curves and pore diameter distributions (insert) of pure g-C$_3$N$_4$ and Ni$_2$P/g-C$_3$N$_4$ samples.

separation of photogenerated electron-hole pairs, which enhances both H$_2$ evolution and PEC performance.

4. Conclusions

In conclusion, noble-metal-free Ni$_2$P QDs modified g-C$_3$N$_4$ is successfully prepared serving as a low-cost, stable and efficient catalyst for photocatalysis and photoelectricity. Noticeably, g-C$_3$N$_4$/Ni$_2$P-3% owns the extremely high H$_2$ evolution rate (1503 μmol h^{-1} g^{-1}) and photocurrent response value (82.58 μA), which are more about 120 times and 11 times than that of pure g-C$_3$N$_4$, respectively. Moreover, the photocatalytic and photoelectric activity of Ni$_2$P/g-C$_3$N$_4$ hybrid is approximately 3 times that of the optimized Pt/g-C$_3$N$_4$, demonstrating transition metal phosphide is desired to become efficient and cheap cocatalyst in replacement of noble metal. The photocatalytic and photoelectric activity of g-C$_3$N$_4$ drastically boosted results from the effective transferred and separated of charge carriers. In addition, the synthesized g-C$_3$N$_4$/Ni$_2$P has been validated to have quite high stability during recycling tests. This work will provide a significant step toward for developing high-efficiency dual functional catalytic materials utilizing low-cost and sufficient elements (C, N, P and Ni) in the world.

Fig. 10. Photoluminescence spectra (a) and fluorescence decay curves (b) of pure g-C$_3$N$_4$ and g-C$_3$N$_4$/Ni$_2$P-3% samples.

Fig. 11. The possible schematic diagram of photocatalysis and photoelectricity over g-C$_3$N$_4$/Ni$_2$P-3% samples.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.apcatb.2018.06.062.

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